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Molecular photochemical thermometers: investigation of microwave superheating effects by temperature dependent photochemical processes

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Abstract

The first study of temperature dependent photochemical reactions in the microwave field is reported. Two different photochemical processes: temperature dependent solvent effects in the Norrish type II reaction and the photo-Fries reaction, were investigated under various thermal conditions including microwave heating. The former process exhibited a linear and reliable temperature dependence which served for the estimation of the microwave superheating effects in four different solvents. Their magnitudes were in a perfect agreement with the measured temperature enhancements. Thus, this photochemical system is proposed as a reliable molecular photochemical thermometer. The latter photochemical reaction studied showed a non-linear temperature dependence. All chemical changes in the microwave field were rationalized as a consequence of thermal effects. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Photochemistry; Microwave; Superheating; Electrodeless discharge lamp; Thermal Effects; Photochemical thermometer

1. Introduction

Microwave (MW) chemistry represents one of the important dimensions of modern chemistry today [1,2]. Microwave heating increases efficiency of many chemical processes at the same time as it can reduce formation of by-products caused by overheating. The magnitude of microwave heating depends on the dielectric properties of the molecules. Chemical processes performed under microwave radiation (microwave chemistry) are believed to be affected by superheating, polarization, dielectric properties, hot spots formation, nuclear spin rotation, and spin alignment [3–5]. Thus, the use of MW irradiation has led to the introduction of new concepts in chemistry. The existence of a “specific microwave effect” in homogeneous reactions, i.e. non-thermal effect, is still a matter of debate. The subject of electromagnetic heating has been reviewed in the recent literature [6–8].

In the past 2 years, we reported on an original photochemical reactor consisting of the electrodeless discharge lamp (microwave lamp; MWL) that generates ultraviolet (UV) radiation in the MW field [9–11]. Such arrangement, in which MWL is placed directly into the reaction vessel in a MW oven, was proposed by Církva and Hájek as a reactor for potential applications in organic chemistry [12]. Microwave photochemistry is otherwise quite a rare topic [13]. Chemat et al. [14] studied the rearrangement of 2-benzoyloxyacetophenone in the presence of bentonite that is sensitive on thermal as well as UV treatment [14]. Some analytical chemistry applications were reported just recently [15,16].

In this paper, results from microwave-assisted photochemistry experiments on the photo-Fries and Norrish type II reactions provide another insight into the subject of microwave heating. A reasoning about the superheating effects on those photoreactions is presented.

2. Results

2.1. Photo-Fries rearrangement

The photo-Fries rearrangement, analogous to the Lewis acid-catalyzed Fries reaction, belongs among the most studied reactions in photochemistry [17,18]. Scheme 1 shows the excitation of phenyl acetate (**1**) to the singlet state that results in homolytic cleavage of the carbonyl–oxygen bond to give a caged radical pair. In-cage recombination as well as recombination of cage-free radicals result in the acyl migration

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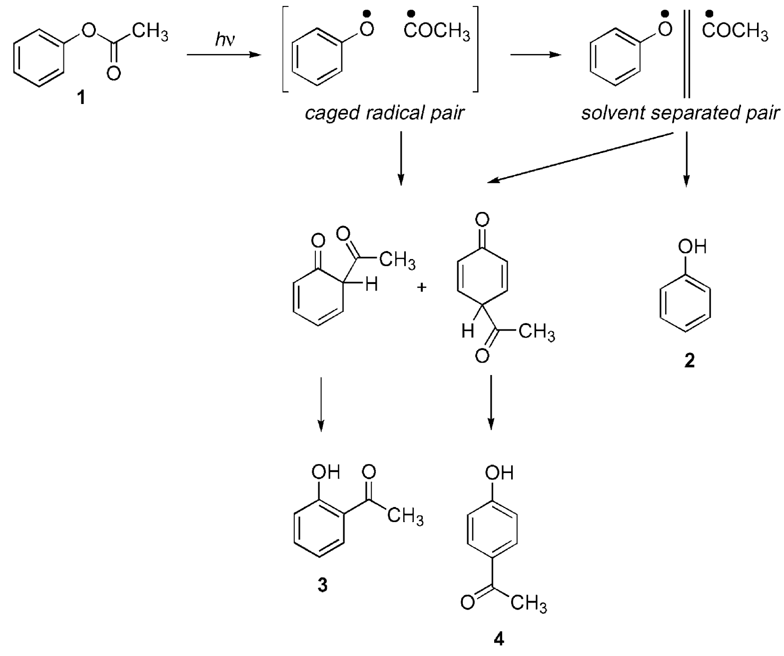


Scheme 1. Photo-Fries rearrangement.

products (**3** and **4**) while hydrogen abstraction by the aryloxy radical leads to the formation of phenol (**2**) [19–21]. The ratio of the *ortho* and *para* products is determined by the electron densities at the corresponding positions in solution, however, the selectivity in organized media, such as zeolites or cyclodextrin, is controlled by other factors [22–24]. The product distribution in various photo-Fries reactions was found to be dependent on temperature, the solvent viscosity as well as the wavelength of incoming radiation [25,26].

Table 1
The photo-Fries reaction in the MW field irradiated at >254 nm[a]

Solvent	Reaction conditions	[**2**]/([**3**] + [**4**])	[**3**]/[**4**]	Temperature (°C)[b]	Superheating effect (°C)[c]
Methanol	COLD	0.21 (0.20)[f]	1.18	20	–
	CONV	0.32	0.95	65	–
	MW, boiling chips[d]	0.30	0.96	66	N.E.[e](1)
	MW	0.35	0.98	71	12 (6)
Ethanol (96%)	COLD	0.16	1.27	20	–
	CONV	0.37	0.96	78	–
	MW, boiling chips[d]	0.39	0.97	81	5 (3)
	MW	0.44	1.01	88	19 (10)
t-Butanol	COLD	0.09	1.39	20	–
	CONV	0.29	1.04	82	–
	MW, boiling chips[d]	0.33	1.03	85	12 (3)
	MW	0.36	1.00	88	22 (6)
Acetonitrile	COLD	0.25	1.65	20	–
	CONV	0.38	1.08	81	–
	MW, boiling chips [d]	0.39	0.98	85	6 (4)
	MW	0.41	0.96	90	14 (9)

[a] Concentrations of phenyl acetate (**1**) were 0.01 mol l^{-1}. A domestic-type microwave oven (Samsung 800 W) applied. The ratios were calculated from the photoproduct concentrations; the reproducibility was ± 6%. COLD: 20°C; CONV: conventionally heated boiling solvent; MW: MW heated solvent. COLD and CONV experiments were irradiated by a conventional medium pressure Hg lamp but MWL was used in the MW experiments.

[b] Temperature measured by the fiber-optic thermometer Nortech ReFlex.

[c] The estimated superheating effects calculated from COLD, CONV, and MW values of the [**2**]/([**3**] + [**4**]) ratios. Numbers in the parentheses are the measured superheating effects by the ReFlex thermometer.

[d] White porcelain chips with hard porous surface were added to decrease the superheating effect.

[e] Not evaluated.

[f] From [22].

For this study, an investigation of the photochemistry of phenyl acetate (**1**) has been conducted under a variety of conditions. The solutions of the compound have been photolyzed (>254 nm) at the temperature range from 20°C to the boiling points of four solvents: ethanol, *t*-butanol, acetonitrile, and methanol under atmospheric pressure. In addition, a set of experiments in the MW field were accomplished using the electrodeless discharge lamp (MWL). All irradiation experiments have been employed in a domestic-type microwave oven.

The results from the ester photolysis are presented in Table 1. The ratio of the photoproduct concentrations [**2**]/([**3**] + [**4**]) represents the acyl separation/migration distribution, while ([**3**] + [**4**]) represents the *ortho-/para-* selectivity of the reaction. We made sure that the reaction conversions in all experiments remained in the range of 20–30%, in which the data were very well reproducible. The values of the ratios were wavelength independent in the range 254–280 nm. In addition, same experimental conditions (amount of solvent, glassware, number of boiling chips, and discharge lamps) were kept in all investigation. Actual ester concentrations in boiling and MW treated mixtures increased by 10–20%, thanks to solvent reflux comparing to 20°C experiments without any apparent effect on the ratios. Any notable effect of a high temperature or MW irradiation on stability of the starting compounds or the products within our experimental conditions have not been observed.

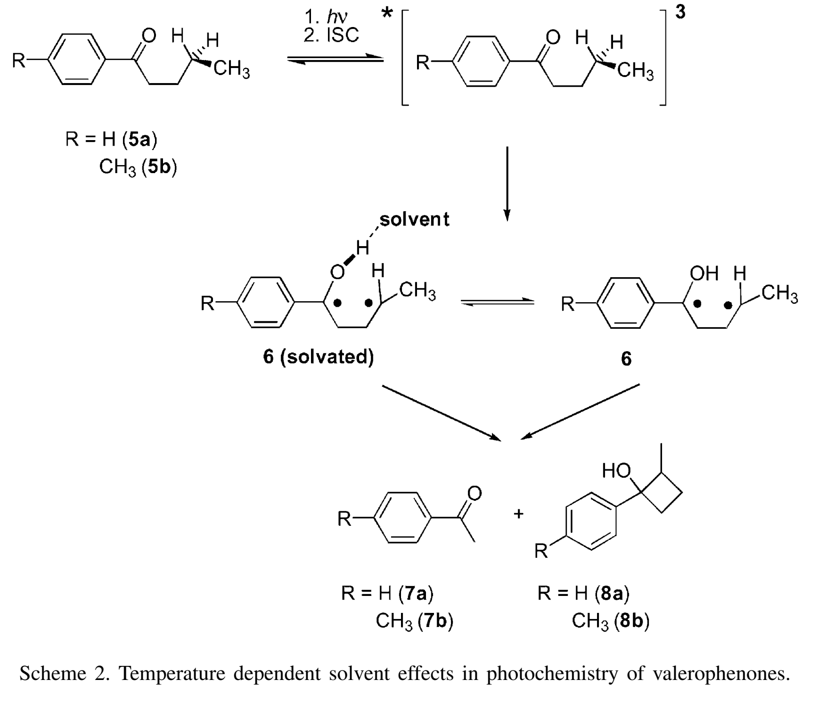
Table 1 lists the calculated superheating effects in the MW field for all solvents. The values have been simply approximated from the ratios at COLD (20°C), CONV (boiling point of the solvent), and MW conditions, assuming that the temperature dependence of [**2**]/([**3**] + [**4**]) is linear. The calculated values are compared to those measured directly by fiber-optic thermometer Nortech ReFlex with a sensor placed directly into the mixture.

2.2. Norrish type II reaction

Excited alkyl phenyl ketones with hydrogen on γ-carbon react on their alkyl chains according to the Norrish type II reaction via the triplet state to produce triplet 1,4-biradicals, which intersystem cross to the short lived singlet biradicals that can cleave, cyclize, or disproportionate back to the starting ketone. Effects of structure and solvation on their photoreactivity have been extensively studied over 4 decades [27–30]. Comparatively few reports dealt with temperature effects on the course of this reaction [31–33].

We recently investigated temperature dependent solvent effects on the Norrish type II reaction (Scheme 2) of valerophenone (**5a**) and its *p*-methyl derivative (**5b**) [34]. Such a small structure change as the *p*-methyl substitution in valerophenone altered the temperature dependent photoreactivity in presence of weak bases. The experimental results suggested that the hydrogen bonding between the type II biradical intermediate (**6**) OH group and the solvent is weaker for *p*-methylvalerophenone than that for valerophenone at 20°C but the interactions dramatically decrease for both ketones at 80°C.

For this work, equimolar mixtures of both ketones were irradiated at >280 nm in various solvents; such an experimental arrangement guaranteed identical photochemical conditions for both compounds. Chemical yields of acetophenone (**7a**, R=H), 4-methylacetophenone (**7b**, R=CH_3), and both cyclobutanols (**8a**, **b**) were monitored. The



Scheme 2. Temperature dependent solvent effects in photochemistry of valerophenones.

Table 2
The Norrish type II reaction in the MW field irradiated at >280 nm

Solvent	Reaction conditions	R^a	Temperature (°C)[b]	Superheating effect (°C)[c]
Methanol	COLD	2.25	20	–
	CONV	1.52	65	–
	MW, boiling chips[d]	1.46	67	4 (2)
	MW	1.34	75	11 (10)
Ethanol (96%)	COLD	2.06	20	–
	CONV	1.30	78	–
	MW, boiling chips[d]	1.26	80	3 (2)
	MW	1.17	91	10 (13)
t-Butanol	COLD	1.90	20	–
	CONV	1.25	82	–
	MW, boiling chips[d]	1.23	84	2 (2)
	MW	1.21	88	4 (6)
Acetonitrile	COLD	2.12	20	–
	CONV	1.12	81	–
	MW, boiling chips[d]	1.03	84	4 (5)
	MW	0.98	90	9 (9)

[a] Equimolar mixtures ($0.01\,\mathrm{mol\,l^{-1}}$) of both ketones used. A domestic-type microwave oven (Whirlpool 900 W) applied. The ratios were calculated from the photoproduct concentrations; the reproducibility was ±6%; $R = ([\mathbf{7a}]+[\mathbf{8a}]/[\mathbf{7b}]+[\mathbf{8b}])$. An external source of UV radiation (200 W) was used.

[b] Temperature measured by fiber-optic thermometer Nortech ReFlex.

[c] The estimated superheating effect calculated from COLD, CONV, and MW values of ratios *R*. Numbers in the parentheses are the measured superheating effects by the ReFlex thermometer.

[d] White porcelain chips with hard porous surface were added to decrease the superheating effect.

fragmentation/cyclization ratio ([**7**]:[**8**]) varied form 5 to 8 and was characteristic for given reaction conditions. We recently showed [34] that photochemical efficiency ratios *R*

$$R = \left(\frac{[\mathbf{7a}] + [\mathbf{8a}]}{[\mathbf{7b}] + [\mathbf{8b}]}\right)$$

are temperature dependent and that the magnitude of the dependence is most likely related to the solvent basicity. Acetonitrile and ethanol were reported to have the largest effects. Now we utilized this photochemical system to our microwave experiments. It is quite clear that the ratio *R* is wavelength sensitive because the absorption characteristics of both valerophenones are different [34]. That is why an external source of UV radiation has been used in order to guarantee that the solutions are photolyzed under the same photochemical conditions. Such an arrangement is similar to that of Chemat's [14]. Table 2 shows results from Norrish type II experiments and the superheating effects for each solvent were calculated similarly as in case of photo-Fries reaction — by approximation from the ratios *R* at COLD, CONV, and MW conditions. The table includes the measured values by ReFlex thermometer again.

3. Discussion

3.1. Superheating

Superheating of solvents at atmospheric pressure, i.e. having the average temperatures higher than those of the corresponding boiling points, has been rationalized by Baghurst and Mingos as a consequence of the microwave dissipation over the whole liquid volume [35]. Nucleation points necessary for boiling are absent here and the loss of heat occurs at the liquid/reactor wall or liquid/air interfaces. Superheating by microwave irradiation is most likely responsible for most reaction efficiency enhancements reported in the literature [8,36–40]. Gedye and Wei, for example, studied several different thermal reactions under CONV and MW conditions under atmospheric pressure [41]. Rate enhancements by factors of 1.05–1.44 have been observed when experiments were accomplished in a domestic-type MW oven but were not observed in a variable-frequency microwave reactor. The enhancement was interpreted as a consequence of solvent superheating or hot-spot formation rather than non-thermal effects. Similar results were reported by Stadler and Kappe in an interesting study of MW mediated Biginelli reaction and the rate enhancements were rationalized in terms of thermal effect as well [42]. Other examples of MW-assisted rate enhancement thanks to solvent superheating by factors below 1.24 were reported on several reactions of organic and organometallic compounds by Gedye et al. [43]. However, some authors discussed that the observed rate (yield) enhancements in microwave-assisted transformations in comparison to conventional heating that are not fully understood. They explained the deviations by the existence of a specific "non-thermal microwave effect" when the results could not be rationalized as a simple consequence of the microwave superheating [2,8,44,45].

We present the first attempts to evaluate MW superheating by means of a temperature dependent photochemical process in this paper. For that purpose, both the well-known

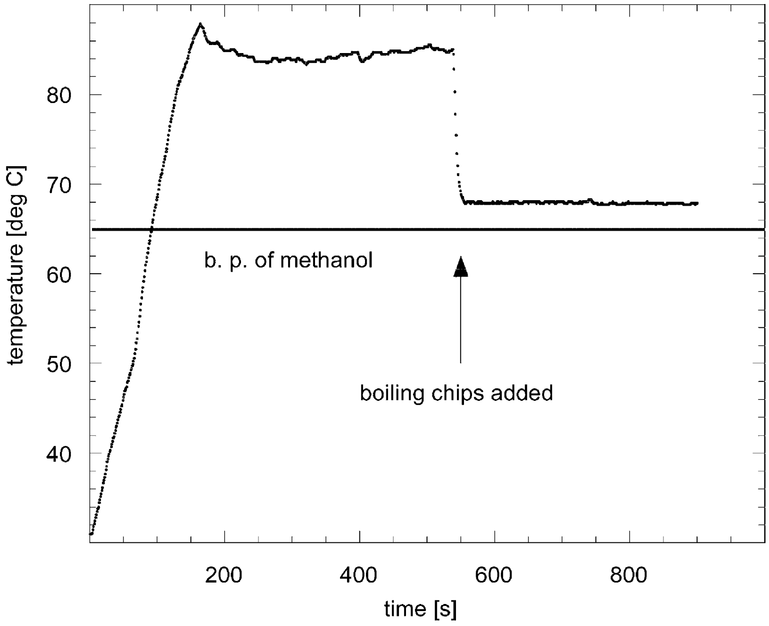


Fig. 1. Temperature profile for methanol showing a dramatic decrease in temperature when boiling chips were added. Measured in the Synthewave 402 microwave reactor with MW power adjusted to 30 W.

photo-Fries reaction and solvent effects in Norrish type II reaction have been successfully employed. Both systems provide "clean" photochemistry without any production of unwanted by-products and offer a unique opportunity to study chemical behavior over a wide temperature range including MW conditions. Unlike the Chemat's report on reactions sensitive to both thermal and MW activation [14], our reaction systems are purely photochemical, thus, no direct thermal activation is present. All solvents used, ethanol ($\mu = 1.66\,\mathrm{D}$), methanol ($\mu = 2.85\,\mathrm{D}$), *t*-butanol ($\mu = 1.64\,\mathrm{D}$), and acetonitrile ($\mu = 3.44\,\mathrm{D}$), are polar, thus easily heated by MW radiation.

In order to support our assumption that the photochemical changes occurring under MW irradiation are caused by thermal activation only and that the boiling chips have a moderate effect on superheating, temperature of MW treated pure solvents was examined using the monomode Synthewave 402 microwave reactor [46]. The temperature/time dependencies, measured by calibrated IR pyrometer, for methanol and acetonitrile are shown in Figs. 1 and 2. The plots clearly depict a rapid temperature increase and leveling off to a plateau regions that corresponds to the superheating effect of 18 and 13°C, respectively. The shape of the curves shows a small temperature enhancement in the beginning of the experiment. At this point, an impulsive and vigorous reflux has been noticed in some cases. Those observations are in a good agreement with other reports [35,47]. When boiling chips were added into a superheated solvent, temperature suddenly dropped to nearly that of the boiling point of a liquid and solvent visually started to boil. It was expected because boiling chips increase the number of nucleation sites, thus reduce the superheating effect [47].

3.2. *Molecular photochemical thermometers*

The results from the study of the photo-Fries reaction clearly depict that the photoproduct ratio, [**2**]/([**3**] + [**4**]), representing the ability of the radical pair to escape from the solvent cage, is strongly temperature dependent. A marked increase in phenol (**2**) formation at the expense of hydroxyacetophenones (**3** and **4**) formation with increasing temperature was anticipated. Weiss et al. showed a similar temperature dependence on 2-naphthyl alkanoate photochemistry [25]. It is clear that phenol could form either by in-cage or out-of-cage processes. The mobility of phenoxy and acyl fragments increase with higher temperature, while the strength of the interactions with the solvent molecules weaken. In addition, the reaction regioselectivity is known to be strongly viscosity dependent [48–50]. On the other side, the [**3**]/[**4**] ratio, representing the *ortho*/*para* selectivity, was not significantly changed in boiling solvents. The small deviations (within several percents) are difficult to interpret and may be explained by the experimental error. The ratio at 20°C shows, on the other side, a significant preference for *o*-acetophenone formation. Mobility of the acyl radical around the phenyl ring probably increases with increasing temperature along with the probability of out-of-cage processes. The different product mix did not support the assumption of a mechanism in which the *ortho*/*para* distribution is only thermodynamically controlled.

Data from the phenyl acetate **1** photochemistry (Table 1) are quite intriguing. The ratio [**2**]/([**3**] + [**4**]) increased going from 20°C to the boiling temperature significantly and the change was characteristic for each solvent. Further increase by factors of 1.09, 1.19, 1.24, and 1.08 in methanol,

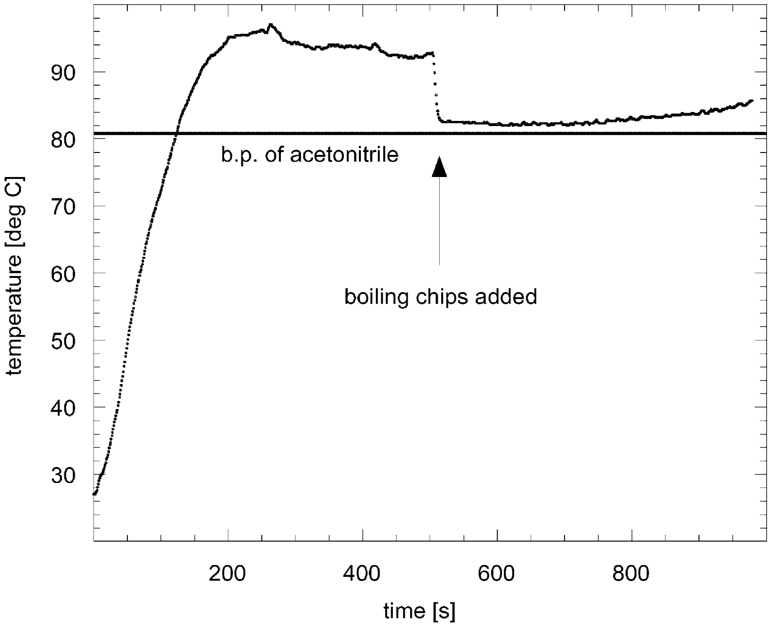


Fig. 2. Temperature profile for acetonitrile showing a dramatic decrease in temperature when boiling chips were added. Same conditions as in Fig. 1.

ethanol, *t*-butanol, and acetonitrile, respectively, was found when the conventional heating was replaced by MW heating. Provided that this change in photochemical regioselectivity by MW treatment originate only from thermal effects, we can estimate temperature increase from COLD, CONV, and MW values of the [**2**]/([**3**] + [**4**]) ratios. Since the temperature dependence of this photo-Fries system was found to be not linear (Fig. 3), the values are somewhat vague; the actual superheating effects must be smaller than those listed in Table 1 (12–22°C). According to the temperature dependencies from COLD to CONV, we expect the superheating effect to be smaller by a factor of 2. This was supported by temperature measurements which revealed that superheating of the mixtures did not exceed 10°C. Introducing boiling chips caused the ratio decrease which is consistent with the observations in pure solvents (Figs. 1 and 2).

We were also intrigued whether MWL, a source of heating itself [9,10], has any influence on the mixture temperature, i.e. on the course of the reaction. Measurements by ReFlex thermometer showed that while the lamp causes faster solvent heating, it does not affect the magnitude of the superheating effect.

A different temperature sensitive photochemical process, the Norrish type II reaction, has been designed. The data from Table 2 clearly indicates that MW heating affected the photochemical behavior of valerophenones in all solvents. It caused further decrease of R by factors of 1.13, 1.11, 1.04, and 1.14 in methanol, ethanol, *t*-butanol, and acetonitrile, respectively, comparing to conventionally heated mixtures. Those overall changes are lower than those of photo-Fries procedure approximately by a factor of 2. It should be stressed out that solvent effects in the Norrish type II reaction were found to be linear in the studied range of temperatures (Fig. 4), i.e. the superheating effect estimations should be much closer to the actual values. The slope differences for alcohols used (Table 2) (methanol:

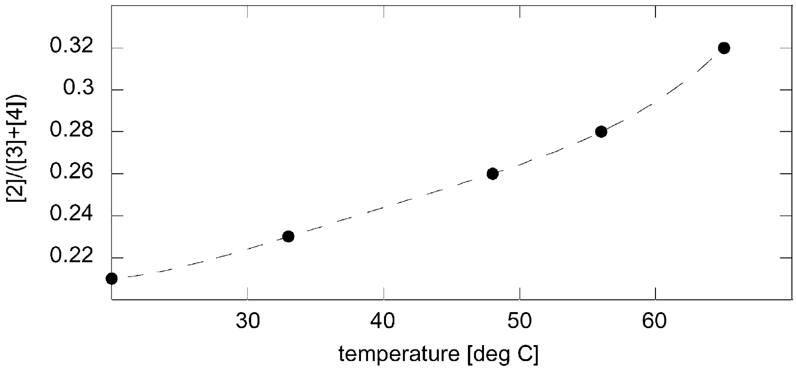


Fig. 3. An example of a temperature dependence of photo-Fries system in methanol.

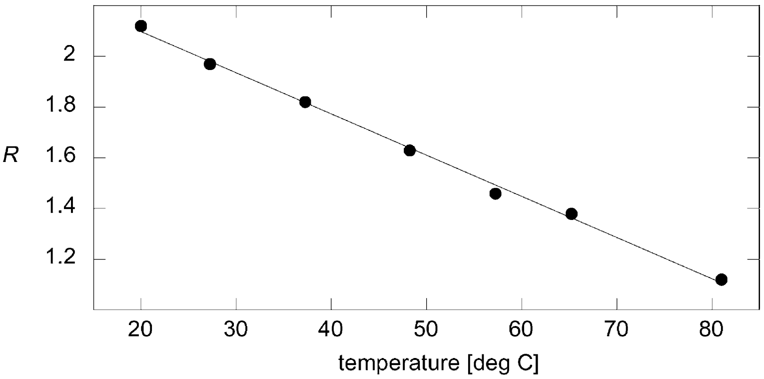


Fig. 4. An example of linear temperature dependence of Norrish type II photochemistry system in acetonitrile.

0.016°C^{-1}; ethanol: 0.013°C^{-1}; *t*-butanol: 0.011°C^{-1}) are probably connected to the steric rather than electronic effects. Table 2 shows a perfect agreement of the estimated values for the superheating effects with those obtained by direct temperature measurements. This surprisingly good resemblance of two independent evaluations of superheating supports our presumption that those photochemical efficiency changes can be rationalized only as a consequence of thermal (i.e. kinetic) effects as opposed to non-thermal effects. To find if our "open-system" system shows a different temperature dependent photochemistry than those in a sealed vessel, investigation of Norrish type II reaction was carried out in acetonitrile from 20 to 100°C. The dependence was curved (less sensitive dependence with increasing temperature) which might be explained by a pressure influence on the biradical solvation. Nevertheless, the ratios R continuously changed over the whole temperature range and the value at 100°C was close ($R = 1.01$) to that measured in the microwave superheated mixture.

Superheating effects 4–10°C are lower than those measured by Baghurst and Mingos [35] who reported the values 19, 24, 14, and 26°C for methanol, ethanol, butanol, and acetonitrile, respectively. Since the magnitude of the superheating effect depends on MW power [42,47], the values higher by a factor of 2 than those listed in Table 2 (but proportionally comparable) are understandable. In addition, the magnitude of 4–24% change in the photoproduct ratios in both our photochemical systems is compared well to the magnitudes of the rate (yield) enhancements of some microwave-assisted thermal organic reactions accomplished under atmospheric pressure [41–43].

In conclusion, the Norrish type II reaction provides a reliable strategy for an estimation of the microwave superheating effects. Since their magnitudes in four different solvents are in a perfect agreement with the measured temperature enhancements, the photochemical system is proposed as a reliable molecular photochemical thermometer. The other photochemical reaction studied, the photo-Fries rearrangement, showed a non-linear temperature dependence which excluded the opportunity to accurately evaluate the microwave superheating effects. All results lead us to the assumption that the photochemical changes occurred only thanks to thermal activation.

4. Experimental section

4.1. Equipment

^{1}H and ^{13}C NMR spectra were obtained for solutions in $CDCl_3$ on an Avance Bruker DRX 500. Gas chromatography was achieved on a Shimadzu GC-17A apparatus and a GC/mass system TRIO 1000 (FISONS Instruments).

MW experiments were accomplished at 2450 MHz frequency in the modified MW oven Samsung M746 (800 W [51]) described elsewhere [10,11] or the Whirlpool M401 (900 W [51]) which had a window for UV irradiation from a conventional Hg discharge lamp. Temperature inside the mixtures was measured by the fiber-optic thermometer Nortech ReFlex with an ultrafast miniprobe. The external irradiation guaranteed identical photochemical conditions for the experiments. The microwave equipment must operate within the safety limits prescribed locally in the country of installation [11,52]. The limit on the safe stray leakage of microwave power density was kept below 5 mW cm^{-2} at 2450 MHz measured in the 50 mm distance from the equipment [53]. It was extremely important that the equipment was checked for leaks especially around the modified area. Some studies were also conducted in the microwave monomode reactor Synthewave 402 (Prolabo) [46] equipped with an IR pyrometer, quartz reaction vessel, and a cooling system. This microwave reactor operated with maximum 300 W output power at 2450 MHz frequency.

The MWL were manufactured in Teslamp (Prague, Czech Republic). The lamps were made of 9 mm quartz tubing (of approximately 1 mm thick glass) of the 13 mm length, filled with mercury and argon, and sealed under 20 Torr vacuum. Quartz absorbs most of UV irradiation below 250 nm.

4.2. Chemicals and solutions

Valerophenone (>99%) was obtained from Aldrich Chemical Co. and was further purified by distillation under reduced pressure. *p*-Methylvalerophenone was synthesized from *p*-methylbenzonitrile and butylmagnesium bromide according to the Wagner's procedure [34,54] and was purified by distillation under reduced pressure. Phenyl acetate (>99%) was purchased from Aldrich and was used as received. Hydroxyacetophenones (>98%) were purchased from Aldrich and served as analytical standards as received. Hexadecane (>99%) from Schuchardt and octadecane (>99%) from VUSPL, Pardubice were used as received as the internal standards in the GC analyses. All solvents were purified by standard procedures.

4.3. Microwave and irradiation experiments

All solutions were prepared directly by weighing the desired material into volumetric flasks or by dilution of stock solutions. Solution mixtures were degassed by bubbling the solutions with argon for 15 min. The Norrish type II reaction experiments were accomplished in the MW oven with an external source of UV radiation (200 W high-pressure Hg discharge lamp; the necessary irradiation time was usually 0.1–0.5 h) in the same Simax vessels under argon atmosphere. Simax (Pyrex equivalent) absorbs most of UV irradiation below 280 nm. Conventional heating in the oven was enabled by a heating plates (Omega) placed under the glass vessel.

Photochemical photo-Fries reaction experiments at temperatures below the boiling points of the solvents were accomplished under argon using a conventional medium-pressure mercury lamp (400 W, Teslamp; the necessary irradiation time was usually 2–4 h) with a quartz filter (>250 nm). The experimental MWL system consisted of an electrodeless discharge lamp placed into the reaction solution in the MW field. We assured that most of the solution was under the direct MW radiation [10]. Circulating cool water or small amount of MW absorbing material removed the excess of microwave power and prevented the magnetron from destruction by overheating. Since MW absorbers may lower the MW efficiency of the reactor, the same amount of the material was used for a good experimental reproducibility. However, water can conduct MW radiation, thus it was necessary that the equipment was checked for leaks. Working with superheated flammable and toxic solvents in a microwave reactor needs a special attention [11].

4.4. Photoproduct identification and analysis

Photo-Fries [17,22] rearrangement photoproducts were analyzed by GC/MS and GC methods. Identification of the products was based on comparison of their mass spectra and retention times with those obtained from authentic samples. Traces (<1%) of anisole and *m*-hydroxyacetophenone were observed.

The only photoproducts followed for all reactants in Norrish type II studies were acetophenones and cyclobutanols. Formation of a minor photoproduct (<2% yield, assuming the same GC response factor as valerophenone) was also observed and it was believed to be 1-arylcyclopentanol as it was described elsewhere [32,27]. Identification of acetophenones and starting valerophenones, isolated by flash chromatography, was based on ^{1}H NMR, ^{13}C NMR, and on GC comparisons with authentic samples (Aldrich). Cyclobutanols were identified using GC and GC/mass instruments as reported before [34]. The same analysis was accomplished for *p*-methylvalerophenone [33,34]. Each sample was analyzed three times; in case that the values differed by more than 6% the measurement was repeated.

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